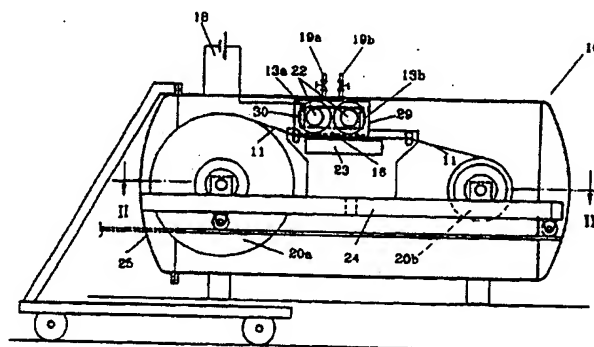


PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6: C23C 14/08, 14/56, 14/35, F24J 2/48	A1	(11) International Publication Number: WO 98/11271 (43) International Publication Date: 19 March 1998 (19.03.98)
(21) International Application Number: PCT/SE97/01545 (22) International Filing Date: 15 September 1997 (15.09.97) (30) Priority Data: 9603393-1 16 September 1996 (16.09.96) SE (71) Applicant (for all designated States except US): SCANDINAVIAN SOLAR AB [SE/SE]; Stora Ävägen 1, S-436 34 Askim (SE). (72) Inventor; and (75) Inventor/Applicant (for US only): HULTMARK, Göran [SE/SE]; Väbelgatan 6, S-426 76 Västra Frölunda (SE). (74) Agent: GÖTEBORGS PATENTBYRÅ; P.O. Box 5005, S-402 21 Göteborg (SE).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> <i>In English translation (filed in Swedish).</i>

(54) Title: A METHOD FOR MANUFACTURING AN ABSORBENT LAYER FOR SOLAR COLLECTORS, A DEVICE FOR PERFORMING THE METHOD AND AN ABSORBENT LAYER FOR SOLAR COLLECTORS

**(57) Abstract**

Process and plant for the manufacture of a spectral selective absorbing layer on solar collectors having a high solar absorption ability and a low thermal emittance. The process takes place on a movable receiving material by atomizing metal in a coating zone (16) present in a chamber using a sputtering atmosphere, which contains at least one gas supporting the sputtering, preferably argon (Ar) and one reactive gas, preferably oxygen (O). The metal forms the cathode and the receiving material (11) forms the anode, between which a potential difference is obtained and thereby a plasma, whereby metallisation of the receiving material (11) is obtained by sputtering. The reactive gas and the distribution thereof in the coating zone (16) provides that the metal layer deposited onto the receiving material (11) partly oxidizes during the deposition. Hereby a layer is obtained that comprises a grain mixture of metal and metal oxide, whereby metal is embedded into the metal oxide closest to the receiving material, which metal is successively decreased to about zero at the surface of the layer by increasing the addition of oxygen at the end of the coating zone (16). The invention further comprises the layer as such.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon	KR	Republic of Korea	PL	Poland		
CN	China	KZ	Kazakhstan	PT	Portugal		
CU	Cuba	LC	Saint Lucia	RO	Romania		
CZ	Czech Republic	LI	Liechtenstein	RU	Russian Federation		
DE	Germany	LK	Sri Lanka	SD	Sudan		
DK	Denmark	LR	Liberia	SE	Sweden		
EE	Estonia			SG	Singapore		

A method for manufacturing an absorbent layer for solar collectors, a device for performing the method and an absorbent layer for solar collectors

- 5 The present invention relates to a method and device for manufacturing spectral selectively absorbing layers for solar collectors having a high absorbing ability and low thermal emittance on a movable receiving material by sputtering of metal in a coating zone having a sputtering atmosphere comprising at least one gas supporting the sputtering, preferably argon, (Ar), and a reactive gas, preferably oxygen (O_2), whereby the metal constitutes the
- 10 cathode and the receiving material constitutes the anode, between which a potential difference is obtained and thereby, a plasma, whereby metallisation of the receiving material is obtained by sputtering.

BACKGROUND OF THE INVENTION

- 15 Solar collectors having a high energy efficiency absorb the solar radiation falling in thereon, transform it to heat energy, and deliver the thermal energy to a heat exchanging medium with least possible losses.

- The most critical part of a solar collector having high energy efficiency is its absorbing
- 20 surface, which has to be spectral selective, i.e. have the ability of absorbing radiation in the wave length range of 0.3 to 2.5 micrometer, where the substantial part of the solar radiation energy is present. It shall further possess a low thermal emittance in the wave length range of 4.0 to 50 micrometer.

- 25 A number of methods are known to obtain reflecting surfaces on e.g. A solar collector, viz., anodization with a subsequent metal pigmentation and sputtering or atomizing.

- Sputtering is obtained by means of having the cathode bombed by ions in a plasma gas formed by a potential difference between the cathode and the receiving material, whereby
- 30 the cathode material is being atomized and the material forms a coating upon the receiving material. The process takes place in a vacuum chamber.

Solar energy absorbing means are known from SE-C-7713121-7, which means comprises a sheet formed element of aluminum sheet and a surface layer applied upon this by means of anodizing, surface layer has a high spectral selectivity and which consists of an aluminum oxide layer having been tightened afterwards and having a maximum thickness of 1.5 micrometer. The surface layer comprises small pores comprising metal, which layer is completely included into the oxide layer and are isolated from each other. The manufacture of the absorbing surface takes place using anodization and introduction of metal into the pores in an electrolytic way. This method is carried out in two different process steps and two different metals are used. The methods are labour intense and requires a lot of man power. After the electrolytic treatment a number of environmentally dangerous residual products are produced which have to be safely stored and destructively treated.

Further, from US-A-4,964,963 there is known a method using two process steps, whereby a solar energy reflector is primarily coated with a stainless steel in an oxidizing atmosphere by atomizing whereupon a second metal layer having a high reflecting ability is atomized above the steel.

From US-A-4,990,234 and the international application WO 87/06626 there is known different methods for coating glass surfaces with another material, by means of the atomizing technology.

DE-3,022,714-C2 describes a method for the preparation of a selectively absorbing layer for a solar collector using an argon-nitrogen sputtering atmosphere, where nickel is transferred to nickel nitride by means of cathode atomizing. The process provides a surface having high absorption values and a relatively low thermal emittance, but it is not suited for industrial manufacturing as the treatment time (30 min for a treatment surface of 1.6 m²) during the atomizing is far too long.

THE OBJECT OF THE INVENTION AND ITS MOST IMPORTANT FEATURES

The object of the present invention is to obtain a spectral selective absorbing surface on solar collector elements, which surface has a very high solar absorbing ability, in the range of 96 to 97 % and having a low thermal emittance, in the order of 10 %, and which can be

produced with high capacity in industrial scale. These objectives have been solved by the fact that the reactive gas in an amount of 1 to 50 cm³/min, kW, preferably 10 cm³/min, kW and the distribution hereof in the coating zone, provides that the metal layer deposited onto the receiving material partly oxidizes during the deposition, whereby a layer is obtained that comprises a grain mixture of metallic material and metal oxide, whereby 40 to 80 %, preferably about 50 %, of metallic material is embedded into the metal oxide closest to the receiving material, which metallic material is successively decreased to about zero at the surface of the layer by increasing the addition of oxygen at the end of the coating zone, that the metal is selected from the group consisting of nickel, chromium, cobalt, molybdenum, or the similar, or a mixture thereof, preferably a nickel-chromium-alloy where the ratio of chromium is 4 to 30 %, preferably about 20 %, and that the grain size is <0.005 micrometer, preferably 0.001 micrometer.

By using the method of the invention the man power demand is reduced with about 60 %. No environmentally dangerous residual products is produced at the sputtering. The manufacturing time, the manufacturing costs, and material and energy consumption can be reduced.

DESCRIPTION OF THE DRAWINGS

The invention will be described in the following with reference to the exemplifying embodiment shown in the accompanying drawings.

Fig. 1 shows diagrammatically a cross-section of an exemplifying embodiment of a sputtering plant of the invention.

Fig. 2 shows a cross-section along the line II-II of Fig. 1.

Fig. 3 shows a cross-section of a second exemplifying embodiment of a sputtering plant of the invention.

Figs. 4-6 show three different cross-sections IV-IV, V-V, and VI-VI of the exemplifying embodiment of Fig. 3.

Fig. 7 shows a graph of the cathode characteristics.

DESCRIPTION OF EXEMPLIFYING EMBODIMENTS

Figs. 1 and 2 show a pressure vessel or vacuum container 10 comprising a controlled atmosphere, which container 10 is intended for the sputtering process of the invention. The chamber 10 comprises a number of outlets 21 connected to each their vacuum pump 17 and two inlets 19a and 19b respectively, for each their gas. Within the container 10 a cathode atomizing means 30 is arranged comprising a number of cathodes 13a, 13b connected to at least one energy source, at least one magnetron 22 or the similar, and devices for carrying and feeding the receiving material 11, which is wound onto rolls 20 and 20b in the form of a band.

10 Vacuum is obtained by means of the vacuum pumps 17 decreasing the pressure in the pressure vessel 10 via the outlets 21 until the vacuum as desired has been obtained. The of receiving material 11 which preferably consists of aluminum sheet, but can consist of copper, nickel, or chromium as well, is divided into a number of, e.g., five rolls, for each batch of treatment which rolls are stored in a carriage 24 being movable into the container
15 10 from an openable end 25 of the container. Inside the pressure container 10 clutches 26a and 26b are connected to a driving and braking means 28, and 27, respectively, which via the clutches 26a, and 26b, connect the rolls 20a and 20b of the receiving material. The receiving material 11 is rolled off from the roll 20a, is treated in the treatment zone 16, and is rolled onto the roll 20b.

20 The cathode atomizing means 30 is insertable into the container via a channel 29 arranged transversally to the pressure container 10, so that the means is situated in the treatment zone 16. The atomizing means 30 comprises the cathodes 13a and 13b consisting essentially of nickel (Ni) and two magnetrons 22 situated in a short distance from the receiving
25 material 11.

When the carriage 24 with the rolls 20a and 20b placed thereon is situated in the container 10 and this has been sealed and the pressure as desired has been obtained the cathodes 13a and 13b are connected to the energy source 18, while the receiving material 11 is rolled off
30 from the roll 20a to the roll 20b, whereby it passes the treatment zone 16. The cathodes 13 are, in accordance with the present example, cylindrically shaped and are rotating. There is a possibility of lowering the cathodes successively during the ongoing process so that the

material dedepositing rate shall become as even as possible. Simultaneously, a gas mixture consisting of a rare gas, e.g., argon (Ar) and a reactive gas, e.g., (O), is added via the lines 19a and 19b, respectively.

- 5 By means of the potential difference between the cathodes 13, and the receiving material 11 the gas become charged between these and forms a plasma gas. The ion activity of the plasma gas contributes to the fact that the ions of the plasma collide with nickel atoms on the cathode, whereby Ni-atoms are shoot out from the cathode surfaces and are attached to the receiving material. The concentration or amount of oxygen is chosen in such a way
10 that the nickel layer deposd on the receiving material partly oxidizes during the deposition. In such a way a layer is obtained having a grain mixture of metallic nickel and nickel oxide.

- The thickness of the layer is about 0.16 micrometer. In order to obtain a high absorption of the solar radiation a larger amount of metallic nickel should be present closest to the receiving material in order that then successively decrease to almost zero at the surface. This task is solved at a movable receiving material in such a way that more oxygen gas is added at the end of the coating zone than at the beginning thereof. By placing the gas nozzle 23 of the reactive gas at the outlet end of the coating zone and having it turned to form an
20 angle obliquely towards this, a more thorough oxidation is obtained at the end of the treatment zone compared with the beginning of the zone. This means that the ratio of metallic nickel is 40 to 80 %, preferably 50 % closest to the receiving material. The surface layer of the coating consists essentially of oxidized particles.

- 25 The metal oxide (NiO) has a relatively high refraction index, and thus about 7 % of incoming solar radiation is reflected. In order to be able to reduce reflexion losses the surface is coated with a further layer where the oxygen of the plasma has been mixed with a gas, e.g., flourine (F) which forms an oxiflouride (NiOF) having a lower refraction index. The thickness of this layer is about 0.05 micrometer. By means of this step the reflexion losses
30 are reduced to about 2 % for a totally smooth surface.

The embodiment shown in Figs. 3 to 6 differs from the preceding one as the off and on

rolling rolls 20a and 20b, respectively, are placed side by side on the same shaft 35, whereby a more compact design of the pressure container 10 can be obtained.

5 The track from the off rolling roll 20a to the on rolling roll 20b is determined by a number of pulleys 34a - 34d. The receiving material 11 is rolled off from the roll 20a and is conveyed over a first lower pulley 34a, via a second pulley 34b, which with regard to the centre axis of the first pulley 34a is oblique ($\alpha = 9^\circ$), whereupon the material is led over a second upper oblique pulley 34c and a second lower pulley 34d to the on rolling roll 20b. The axis 35 can be connected to a driving means (not shown) via a clutch device 26a. 10 The part of the shaft onto which the on rolling roll 20b is mounted is arranged being driving while the second part onto which the roll 20a is mounted can roll freely, but its rotational speed can be regulated by means of brakes (not shown). The shaft 35, the pulleys 34 and their supporting frame is mounted on a carriage 24 which can be moved in and out from the container 10.

15 Fig. 4, which shows a cross-section along the line IV-IV through the container 10, shows how the cathode atomizing devices 30 are arranged over the track the receiving material 11 passes between the oblique pulleys 34b and 34c. At each cathode atomizing device 30 there is at least one inlet 19a arranged for the addition of a rare gas (e.g., argon) and an inlet 19b for the reactive gas (e.g., oxygen). The container communicates with a vacuum pump 17, which is used to empty the container of air and to obtain a controlled atmosphere. By arranging a number of cathode atomizing devices 30 after each other, the thickness of the oxide layer can be built up, if so wanted, and possibly, several different layers can be applied.

25 The sputtering is preferably carried out in two steps, viz. A first step where the reactive gas is added in a rear end of the treatment zone seen in a transporting direction of the receiving material and in a second step in which reactive gas is added from the opposite direction in the beginning and at the end of the treatment zone. In order to reach an absorption of 96 to 30 97 % an anti reflexion layer (AR-layer) can be applied in step two above the metal oxide, which anti reflexion layer is formed by adding fluorine gas to the reactive gas - oxygen gas. The reflexion is reduced in this way over the total solar wavelength range thanks to

the lower refraction index of the metal fluoride compared to that of the metal oxide.

In the plant according to Fig. 5 heating devices 23 are shown in the form of heating helixes which when needed heat the receiving material 11 when it passes them, as well as cooling devices 32 for cooling the receiving material. The heating 23 and cooling 32 devices have
5 turned out to be superfluous in the operations shown in examples I and II. When using other metals, receiving materials, and gases they may, however, become necessary, to control the (surface) temperature of the receiving material 11. Between each heating and cooling device there is arranged heat sensitive sensors 31 which read the temperature of
10 the receiving material and transmit data to a controlling unit (not shown) which controls the heating helixes and the cooling devices to maintain the correct temperature of the receiving material.

The graph 33 of Fig. 7 shows the relation between the cathode voltage and the oxygen
15 concentration. The most the sputtering process. Before the oxygen gas is added only nickel is sputtered from the c a essential part of the graph is between the points A and D which determine the critical part of thode towards the receiving material 11. Between the points B and C when the concentration of oxygen is optimal, some nickel particles react with the oxygen gas whereby a porous oxide matrix having embedded Ni-particles therein is
20 formed, which particles cover the bottom layer of the receiving material. Between points C and D the formation of the oxide layer takes place.

In order to reduce the soft magnetic properties of the nickel material it will be suitable to use a nickel-chromium-alloy having 4 to 30 % of chromium, preferably 20 %, as
25 cathodes. Also other metals other than nickel and chromium can be used, viz. E.g., cobalt or molybdenum, but with regard to costs, nickel will be preferred.

EXAMPLE I

The example relates to a layer on a movable receiving material, addition of the reactive gas
30 at the end of the coating zone, and a stationary cathode.

In the container 10 a pressure of 3×10^{-3} millibar is obtained. The in effect from the energy

source 18 is 7.5 kW, whereby a voltage of 600 V is obtained in the plasma gas. The flow of argon (Ar) was restricted to 400 cm³/min while the oxygen gas flow was 52 cm³/min. The distance between the cathode and the receiving material was 10 cm. A nickel oxide layer Ni + NiO having the thickness of 160 micrometer was formed on the surface of the receiving material consisting of aluminum (Al). The absorption area of said oxide thickness turned out to have a high - 91 % - solar radiation absorption and a low thermal emission - 10 %. The band speed was 1.5 m/min, not preheating. The magnetron gave a temperature of about 300 °C in the coating zone. The cathode had a diameter of 15 cm.

10 The process parameters according to this experiment were varied in accordance with the below given:

The treatment was carried at a pressure of between 1×10^{-4} Torr and 5×10^{-5} Torr, an ineffect of between 100 W and 1 kW, an inflow of argon (Ar) of between 1.0 cm³/min and 20.0 cm³/min and a temperature of between 200 °C and 500 °C.

15

EXAMPLE II

The surface of Example I was coated with a further coating in a second step in accordance with the following:

Pressure: 3 to 10⁻³ millibar

20 Magnetron effect: 4 kW

Voltage: 300 V

Oxygen gas: 80 cm³/min and 60 cm³/min

Tetrafluoro methane (CF₄): evenly distributed in the plasma

Speed: 1.15 m/min

25

The absorption having this further layer turned out to 96 % of absorption and 10 % of emission.

30 The above parameters are specific for this particular experiment and can be varied considerably with regard to the size of the container, the rolling speed of the receiving material etc..

WO 98/11271

PCT/SE97/01545

9

PAGE INTENTIONALLY LEFT BLANK

LIST OF REFERENCE NUMBERS

	10	Pressure container
	11	Receiving material
5	13a, b	Cathode
	14	Absorption surface
	16	Treatment zone
	17	Vacuum pump
	18	Energy source
10	19a, b	Inlets
	20a, b	Rolls
	21	Outlets
	22	Magnetron
	23	Heating device
15	24	Carriage
	25	Opening
	26a, b	Clutches
	27	Braking means
	28	Driving means
20	29	Channel
	30	Cathode atomizing device
	31	Sensor
	32	Cooling device
	33	Graph
25	34a-34d	Pulleys
	35	Nozzle

CLAIMS

1. Process for the manufacture of a spectral selective absorbing layer on solar collectors having a high solar absorption ability and a low thermal emittance on a movable receiving material by atomizing metal in a coating zone present in a chamber using a sputtering atmosphere, which contains at least one gas supporting the sputtering, preferably argon (Ar) and one reactive gas, preferably oxygen (O), whereby the metal forms the cathode and the receiving material or the chamber forms the anode, between which a potential difference is obtained and thereby a plasma, whereby metallisation of the receiving material is obtained by sputtering,
- 5 **characterized in**
- that the reactive gas in an amount corresponding to 1 to 50 cm³/min, kW, preferably 10 cm³/min, kW and the distribution thereof in the coating zone, provides that the metal layer deposited onto the receiving material partly oxidizes during the deposition, whereby a layer is obtained that comprises a grain mixture of metal and metal oxide, whereby 40 to 80 %, preferably about 50 %, of metal is embedded into the metal oxide closest to the receiving material, which metal is successively decreased to about zero at the surface of the layer by increasing the addition of oxygen at the end of the coating zone,
- 15 that the metal is selected from the group consisting of nickel, chromium, cobalt, molybdenum, or the similar, or a mixture thereof, preferably a nickel-chromium-alloy where the ratio of chromium is 4 to 30 %, preferably about 20 %, and
- 20 that the grain size is <0.005 micrometer, preferably 0.001 micrometer.
2. Process according to claim 1,
- characterized in**
- 25 that the total thickness of the sputtering layer is chosen as a function of the wavelength of the solar radiation within the wavelength range of 0.3 to 4 micrometer, preferably, is a thickness of 0.12 to 0.2 micrometer, suitably 0.16 micrometer, chosen.
3. Process according to claim 1 or 2,
- 30 **characterized in**
- that the receiving material passes through a pressure container (vacuum container 10) using a controlled atmosphere, at a pressure of 1×10^{-4} to 10^{-2} mbar, preferably 6×10^{-3} mbar,

and that at least a part (16) of the receiving material (11) is brought within an activity area before at least one sacrificing cathode (13) connected to an ineffect of 5 to 100 W/cm² of cathode area, preferably 50 W/cm², and which cathode essentially consists of nickel (Ni) and is brought in cooperation with at least one rare gas, preferably argon (Ar) in an amount
5 corresponding to 5 to 100 cm³/min, kW, preferably about 30 cm³/min, kW and said reactive gas.

4. Process according to claim 1 or 2,
characterized in

10 that the psuttering is carried out in two steps, viz. a first step wherein the reactive gas is added at the end of the treatment zone of the first step in the direction for the transport of the receiving material, and a second step wherein the reactive gas is added contra directed at least in the beginning of the treatment zone of the second step.

15 5. Process according to claim 4,
characterized in

that a second layer is applied onto the surface of the coating formed in the first step in a second or next step by adding to the reactive gas a gas which provides the metal oxide a lower refraction index, preferably fluorine gas or chlorine gas.

20

6. Process according to claim 5,
characterized in

that the thickness of the second layer is chosen as a function of the wavelength of the solar radiation within the wavelength range 0.3 to 4 micrometer, preferably a thickness of 0.02
25 to 0.1 micrometer, preferably about 0.05 micrometer, is chosen

7. Plant for the manufacture of a spectral selective absorbing layer on solar collectors having a high absorption ability and a low thermal emittance on a receiving material by atomizing of a metal in a coating zone present in a vacuum chamber using a sputtering
30 atmosphere, which receiving material (11) is windabel onto and windable off from rolls (20a, 20b) present in a pressure chamber (10), in which a treatment zone (16) is arranged through which the receiving material (11) passes on its way nfromn the one roll to the

other,

characterized in

- that a magnetron equipped cathode atomizing device (30) is arranged in, or introduceable into, the treatment zone (16), to which zone lines (19a, 19b) are arranged to lead for the addition of gases, the reactive gas being arranged to be added at the end of the treatment zone by means of a nozzle, which nozzle is directed contrary to the transport direction of the receiving material.

8. Plant according to claim 7,

characterized in

- that clutches (26) are arranged in the pressure container (10) and connected to driving and braking means (27, 28) arranged outside the pressure container for the connection to the rolls (20a, 20b) of the receiving material (11).

9. Plant according to claim 7,

characterized in

- that the rolls (20a, 20b) for the receiving material (11) are arranged on a carriage (24) being introducable into the pressure container,
that the rolls are mounted on a common shaft (35) side by side,
that the carriage is provided with a number of pulleys (34) via which the receiving material (11) passes on its way from the off rolling roll (20a) to the on rolling roll (20b), and
that one or more of the pulleys (34b, 34c) are oblique to guide the receiving material to the respective roll.

10. Spectral selective absorbing layer on solar collectors having a high solar absorption ability and a low thermal emittance, which layer is applicable on a receiving material by atomizing metal in a coating zone present in a chamber using a sputtering atmosphere, which contains at least one gas supporting the sputtering, preferably argon (Ar) and one reactive gas, preferably oxygen (O), whereby the metal forms the cathode and the receiving material or the chamber forms the anode, between which a potential difference is obtained and thereby a plasma, whereby metallisation of the receiving material is obtained by sputtering,

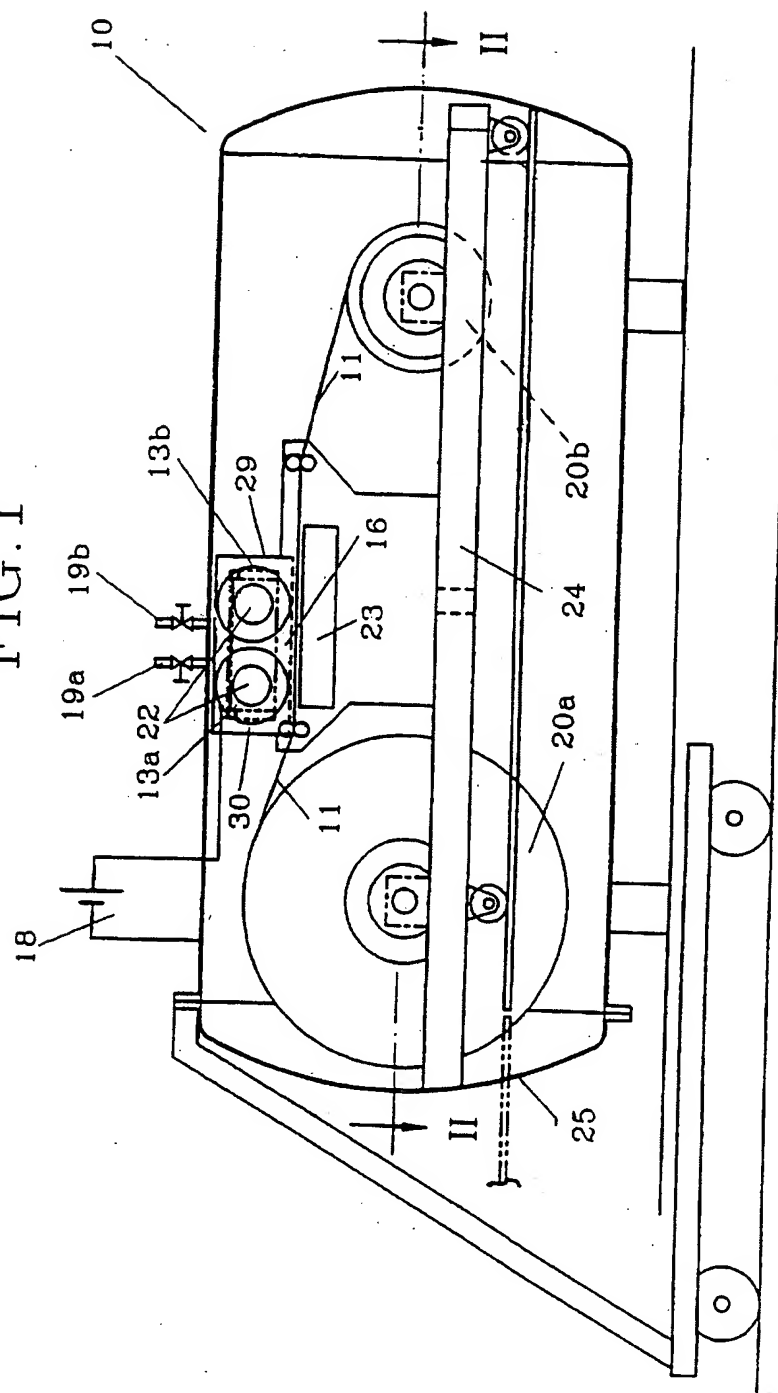
characterized in

- that the reactive gas in an amount corresponding to 1 to 50 cm³/min, kW, preferably 10 cm³/min, kW and the distribution thereof in the coating zone, provides that the metal layer deposited onto the receiving material partly oxidizes during the deposition, whereby a layer
- 5 is obtained that comprises a grain mixture of metal and metal oxide, whereby 40 to 80 %, preferably about 50 %, of metal is embedded into the metal oxide closest to the receiving material, which metal is successively decreased to about zero at the surface of the layer by increasing the addition of oxygen at the end of the coating zone,
- that the metal is selected from the group consisting of nickel, chromium, cobalt,
- 10 molybdenum, or the similar, or a mixture thereof, preferably a nickel-chromium-alloy where the ratio of chromium is 4 to 30 %, preferably about 20 %, and
- that the grain size is <0.005 micrometer, preferably about 0.001 micrometer.

11. Spectral selective absorbing layer according to claim 10,
- 15 characterized in

that a second layer is applied onto the surface of the coating formed in the first step in a second or next step by adding to the reactive gas a gas which provides the metal oxide a lower refraction index, preferably fluorine gas or chlorine gas.

FIG. 1



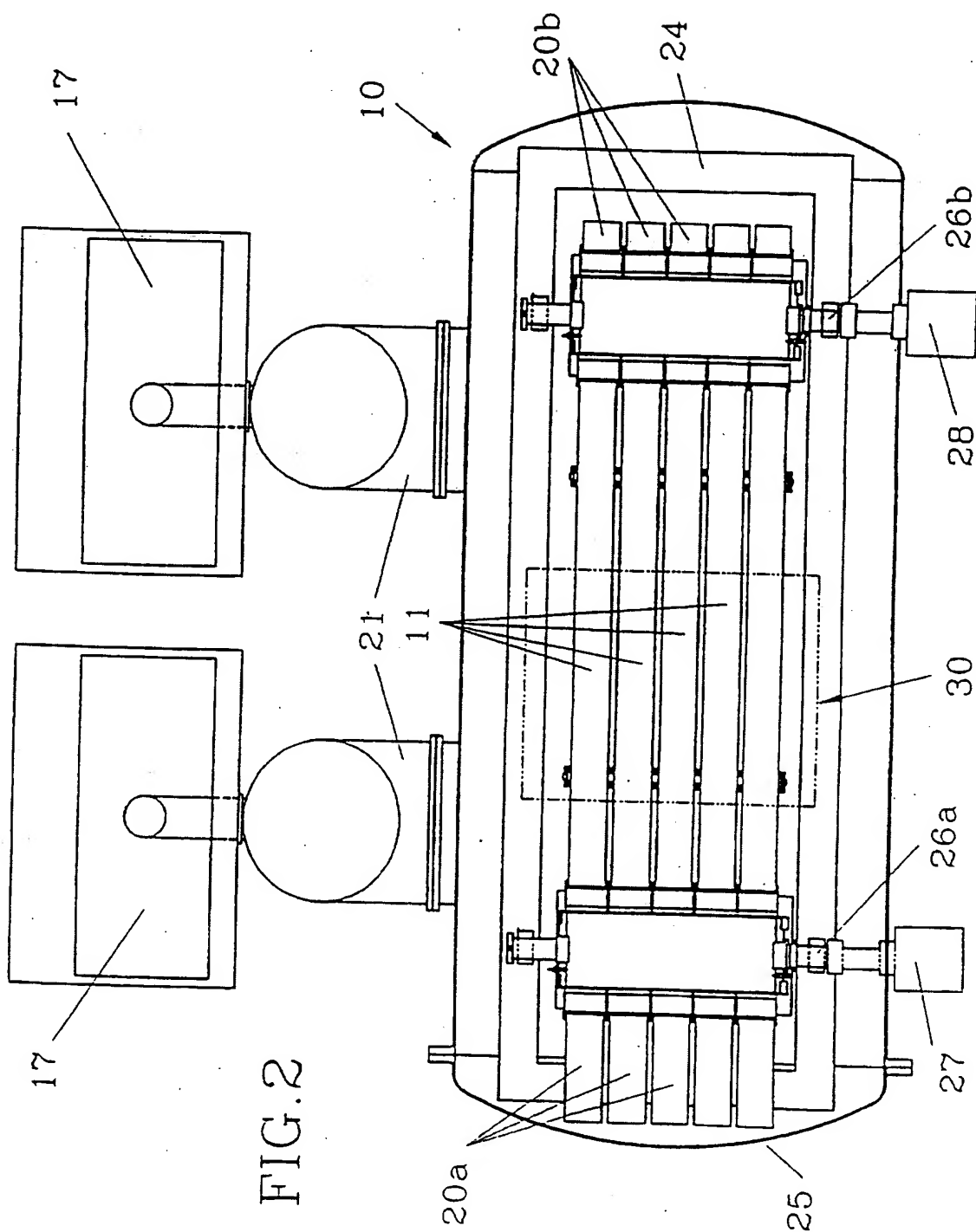


FIG. 3

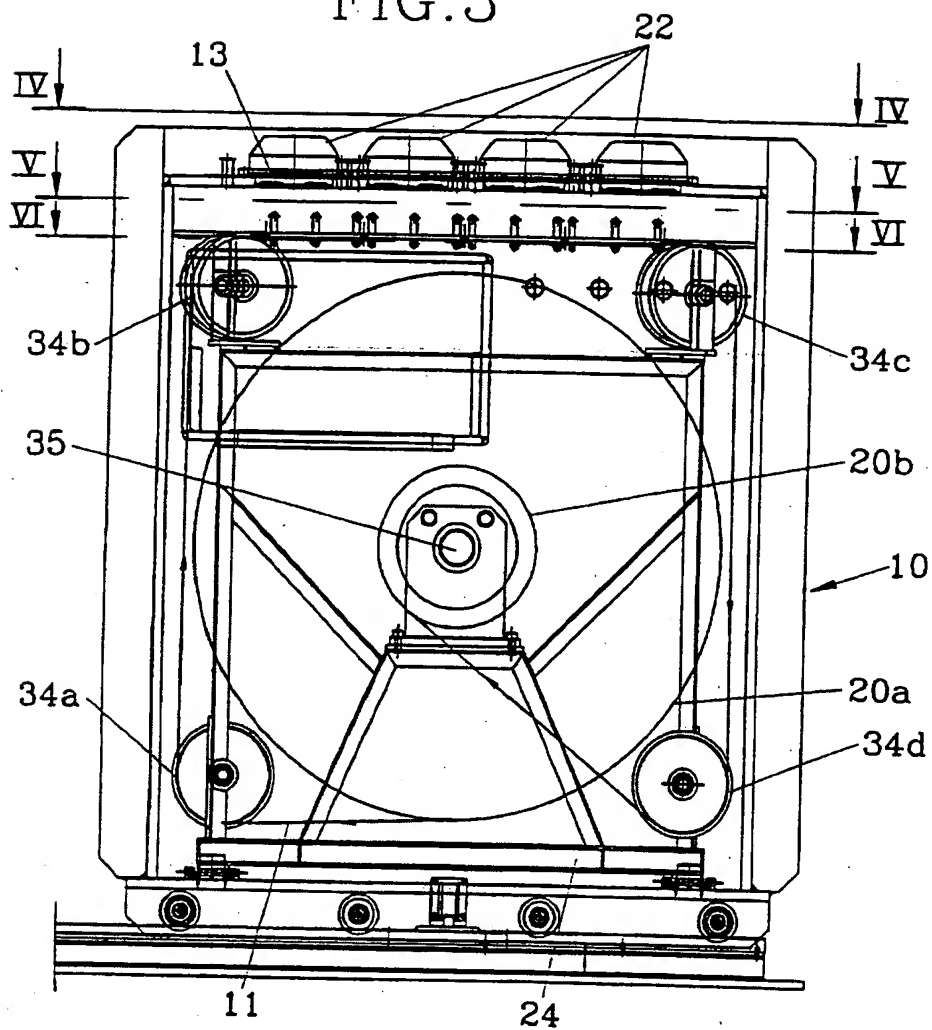
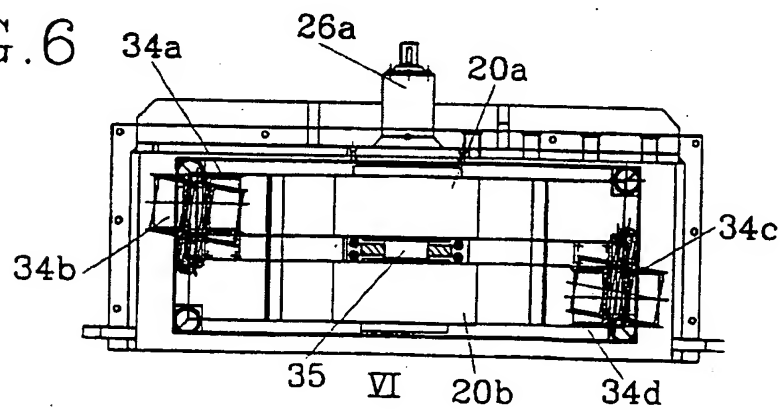


FIG. 6



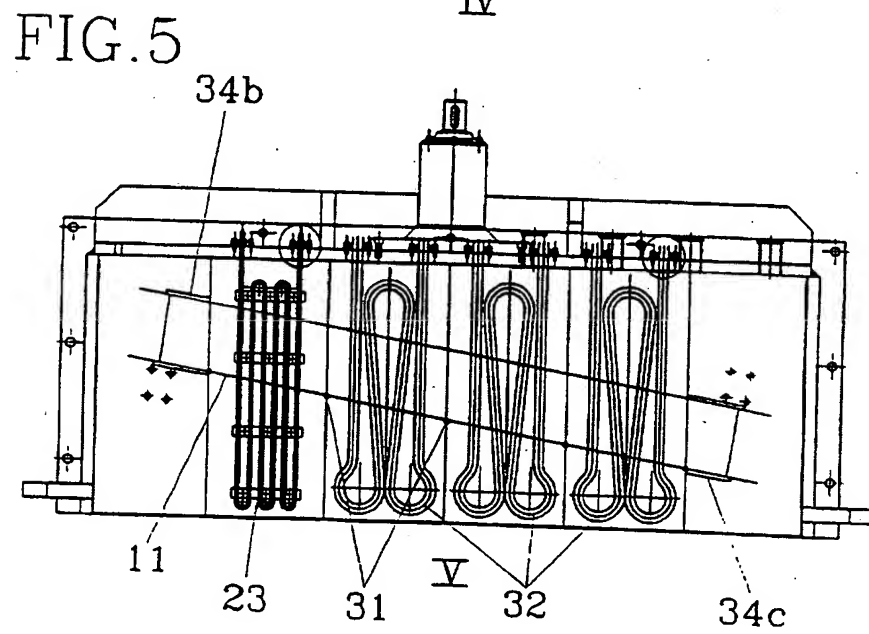
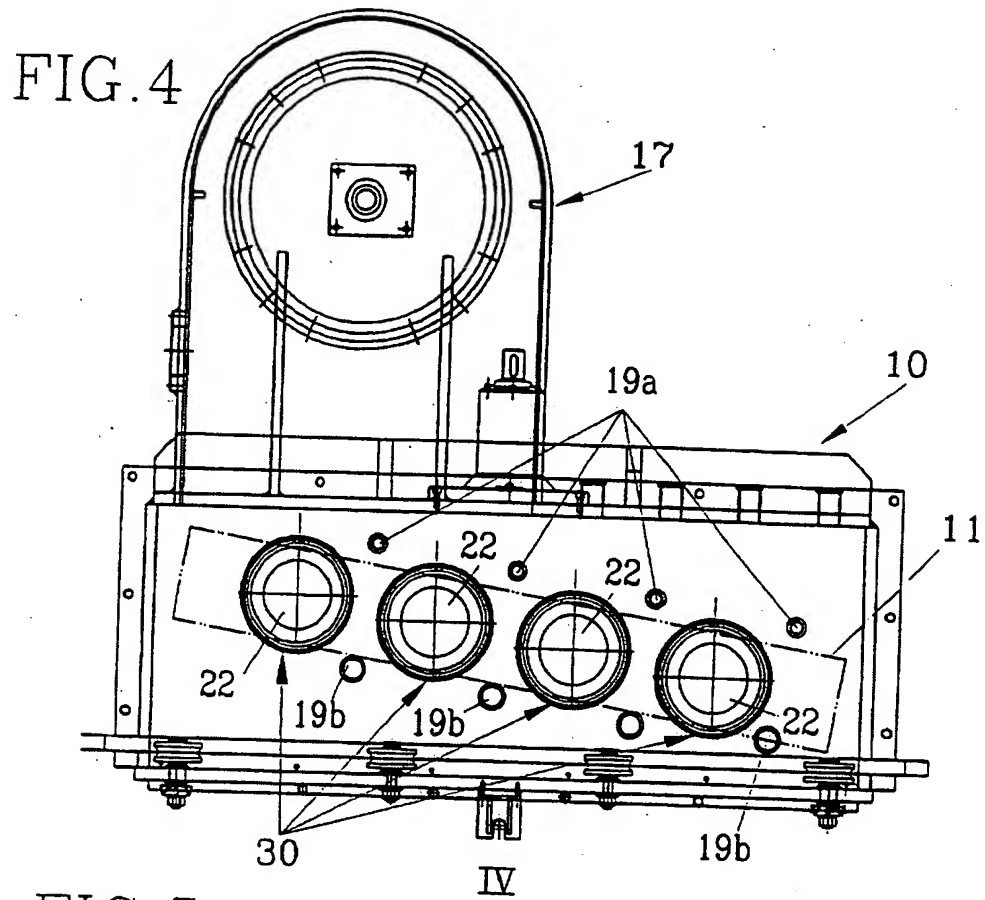
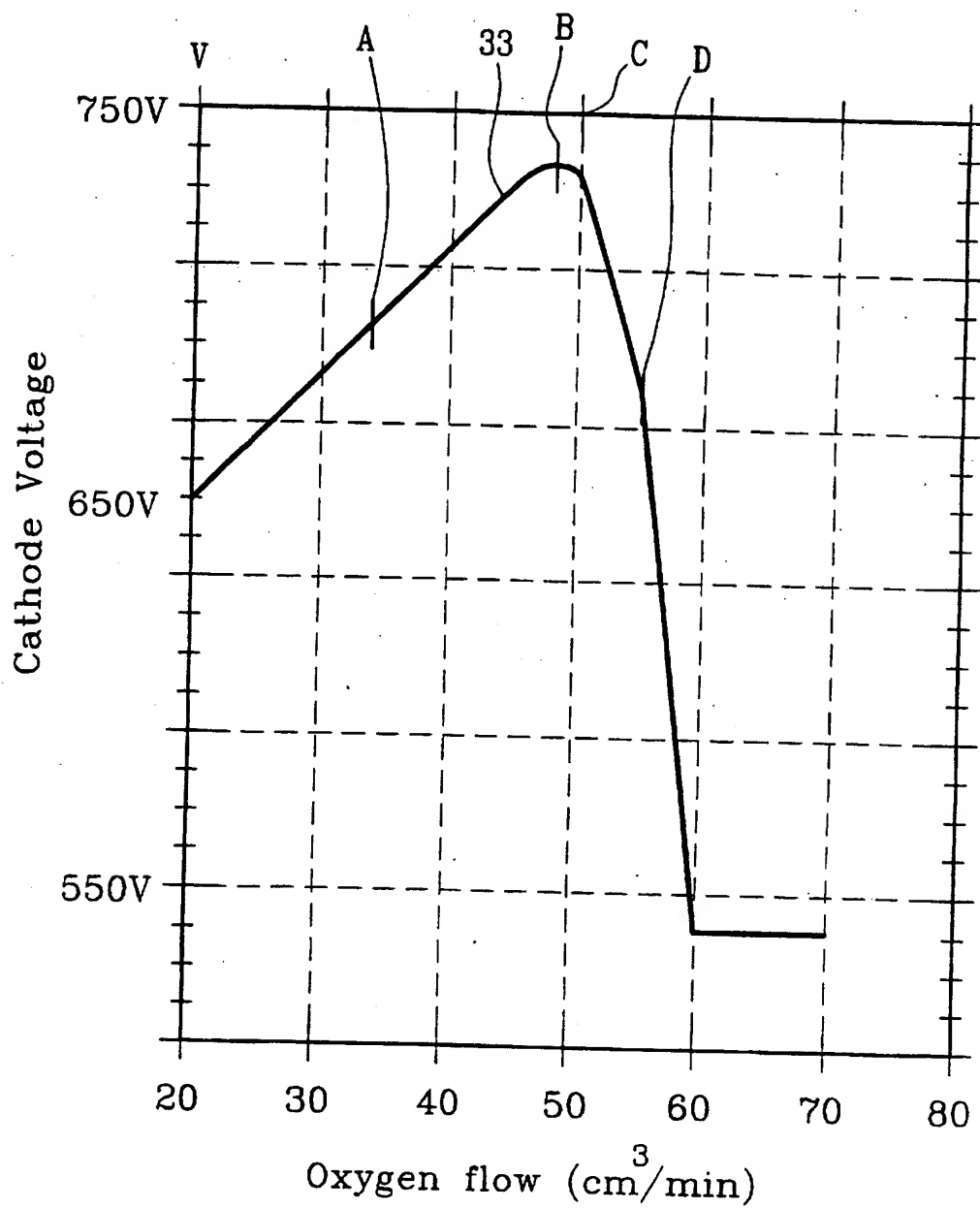


FIG. 7



INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 97/01545

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C23C 14/08, C23C 14/56, C23C 14/35, F24J 2/48
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C23C, F24J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, JAPIO, EDOC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	Dialog Information Services, File 351 DERWENT WPI, Dialog accession no. 003468800 WPI accession no. 82-16744E/09, (AGENCY OF IND SCI TECH), "Forming selective absorption film for solar energy by vacuum plating oxygen-inert gas atmos", & JP, A, 57013172, 820123, 8209 (Basic)	1-11
Y	Patent Abstracts of Japan, Vol 8, No 177, M-317 abstract of JP 59-69658 A (SHIYOUWA ARUMINIUMU K.K.), 19 April 1984 (19.04.84), & JP, A, 59-69658	1-11
Y	DE 3022714 A (BFG GLASSGROUP), 4 March 1982 (04.03.82), column 1, line 1 - line 16; column 3, line 17 - line 22; column 5, line 16 - line 20, column 6, line 17 - line 22, claims 13-15	1-11

☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

<p>* Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>
--	---

Date of the actual completion of the international search

16 January 1998

Date of mailing of the international search report

19 -01- 1998

Name and mailing address of the ISA/
Swedish Patent Office
Box 5055, S-102 42 STOCKHOLM
Facsimile No. +46 8 666 02 86

Authorized officer

Ingrid Grundfelt
Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 97/01545

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4885070 A (GREGOR A. CAMPBELL ET AL), 5 December 1989 (05.12.89), column 3, line 57 - column 4, line 30; column 6, line 29 - column 7, line 15; column 9, line 23 - line 38, claims 1,4 --	4,7-9
Y	WO 9214860 A1 (THE SECRETARY OF STATE FOR DEFENCE IN HER BRITANNIC MAJESTY'S GOVERNMENT OF THE UNITED KINGDOM OF GREAT BRITAIN AND NORTHERN IR...), 3 Sept 1992 (03.09.92), figures 2-4 --	9
Y	WPI/Derwent's abstract, No 95-191241, week 9525, ABSTRACT OF JP, 7110401 (OLYMPUS OPTICAL CO LTD), 950425, & JP, A, 7110401 -----	5,11

INTERNATIONAL SEARCH REPORT
Information on patent family members

02/12/97

International application No.
PCT/SE 97/01545

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 3022714 A	04/03/82	BE 889262 A FR 2486636 A GB 2079323 A	16/10/81 15/01/82 20/01/82
US 4885070 A	05/12/89	AU 2270288 A CN 1033297 A DE 3830478 A EP 0308680 A JP 1108374 A SU 1797629 A	23/03/89 07/06/89 13/07/89 29/03/89 25/04/89 23/02/93
WO 9214860 A1	03/09/92	EP 0581772 A GB 2268192 A,B JP 6505054 T	09/02/94 05/01/94 09/06/94